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## Thermodynamic Model of Aluminum Combustion in SDF Explosions

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### Abstract

*Thermodynamic states encountered during combustion of Aluminum powder in Shock-Dispersed-Fuel (SDF) explosions were analyzed with the Cheetah code. Results are displayed in the Le Chatelier diagram: the locus of states of specific internal energy versus temperature. Accuracy of the results was confirmed by comparing the fuel and products curves with the heats of detonation and combustion, and species composition as measured in bomb calorimeter experiments. Results were fit with analytic functions  $u = f(T)$  suitable for specifying the thermodynamic properties required for gas-dynamic models of combustion in explosions.*

### 1. Introduction

We consider the problem of Aluminum (Al) combustion in Shock-Dispersed-Fuel (SDF) explosions studied experimentally by Neuwald [1]. A two-phase model of this combustion process have been proposed in this 37<sup>th</sup> Conference [2]. Such models require Equations of State (EOS) to describe the fluids [3], [4]. In the 34<sup>th</sup> ICT Conference [5], we proposed the use of the Le Chatelier diagram of Oppenheim [6] to display the loci of states of specific internal energy as a function of temperature to describe the after-burning of PETN, TNT and four other condensed phase explosives with air. We have also used this method to establish the combustion locus in thermodynamic state space [7] for a composite PETN/TNT charge. Here we apply that same approach to Al combustion with air, and we re-visit the TNT case producing a slightly more refined model.

### 2. Le Chatelier Diagram

The thermodynamic states encountered during the explosion of the PETN charge in air are depicted in the Le Chatelier diagram of Fig. 1. These states were computed by the Cheetah code developed by Fried [8]. The locus of states of the Detonation Products–DP lies on the isentrope that starts at the Chapman-Jouguet point CJ and expands down to 1 bar pressure. The heat of detonation is the difference between the energy of the products minus energy of reactants at standard conditions:  $\Delta H_d \equiv u_{0,P-DP} - u_{0,R-DP} = -1,423 \text{ cal/g}_{PETN}$ , and is indicated on Fig. 1. State UV represents the condition found if one detonates the charge adiabatically at constant volume (a so called instantaneous detonation); this gives a

detonation temperature of 4,223 K. If the charge is consumed by a Chapman-Jouguet detonation wave, state CJ is realized with a temperature of 4,600 K. The enhancement of state CJ over state UV is caused by the wave structure coupled with the CJ jump conditions (corresponding to  $\Delta H_d$ ), and is sometimes called the “cold compression energy”. The equilibrium composition of the DP gases changes as they expand down the isentrope; when they reach a temperature of  $T_F = 1,800K$  the composition becomes frozen (point *F*). Note that in this formulation, we neglect the after-burning of the PETN detonation products with air ( $H_c - H_d = 1,916 - 1,423 = 493 \text{ cal/g}_{PETN}$ ). For a 0.5 g PETN and 1-g of Al, this adds about 250 cal/g versus 7400 cal/g from Al combustion, or 3.3%, which is considered negligible in this analysis.

The thermodynamic states encountered during the combustion of the aluminum powder with air are depicted in the Le Chatelier diagram of Fig. 2. The Reactants-R are defined as a stoichiometric mixture of air and Aluminum in *frozen* composition (air/fuel ratio:  $\sigma_s = 4.03$ ). The Products-P are assumed to be in *thermodynamic equilibrium*. These states were calculated with the Cheetah code, assuming  $p = 1 \text{ atm}$ . Computations were also performed assuming combustion at  $p = 10 \text{ atm}$ ; the resulting curve was negligibly different from the 1-atm curve, which was adopted as the standard for this problem. Pressure independence is a perfect gas property of the  $u(T)$  curve, which seems to apply for the present combustion conditions. The heat of combustion is the difference between the energy of the products minus energy of reactants:  $\Delta H_c \equiv u_{0,P} - u_{0,R} = -1,473 \text{ cal/g}_P$  ( $7,409 \text{ cal/g}_{Al}$ ) and is indicated on Fig. 2. Adiabatic combustion corresponds to a material transform from Reactants to Products at constant energy. For Reactants starting at 300 K, this gives a combustion temperature of 3,680 K, as indicated in the figure.

These states have been fit with quadratic functions:

$$u_k(T) = a_k T^2 + b_k T + c_k \quad (k = A, DP, R, P) \quad (1)$$

These functions (curves) do an excellent job at fitting the computed thermodynamic states (data points) as demonstrated in Figs. 1 and 2. The fitting constants are listed in Table 1.

### 3. Pressure

The pressure variation with specific volume along the CJ isentrope was computed with the Cheetah code; results are depicted in Fig. 3. This  $p - v$  relation is fit with the Jones-Wilkins-Lee (JWL) function:

$$p_{JWL}(v, S_{CJ}) = A \exp(-R_1 v) + B \exp(-R_2 v) + \frac{C}{v^{1+\omega}} \quad (2)$$

where  $v$  represents the specific volume ratio:  $v = v/v_0$ . For PETN at  $\rho_0 = 1 \text{ g/cc}$ , the JWL constants are  $A=5.80227 \text{ M-bar}$ ;  $B=0.09301 \text{ M-bars}$ ;  $C=0.01223 \text{ M-bars}$ ;  $R_1 = 7.000$ ;  $R_2 = 1.695$  and  $\omega = \gamma - 1 = 0.246$ . They result in the fit (solid curve) shown in Fig. 3.

Figure 4 displays  $pv/RT$  versus specific volume along the CJ isentrope, as computed by the Cheetah code. For  $v > 28 \text{ cm}^3/\text{g}$ , these values lie on the line  $pv/RT = 1$  representing the perfect gas law. This leads to the following relation for the DP gases:

$$p = \begin{cases} p_{JWL}(v, S_{CJ}) & v \leq 28 \text{ cm}^3/\text{g} \\ \rho RT & v > 28 \text{ cm}^3/\text{g} \end{cases} \quad (3)$$

#### 4. Equations of State

The temperature of the gas for a pure component  $k$ , is computed from the specific internal energy relations shown in Figs. 1 and 2 (that is by inverting eq. (1)) to find:

$$T_k = [-b_k + \sqrt{b_k^2 - 4a_k(c_k - u_k)}]/2a_k \quad (4)$$

Given the temperature, the pressure is found from the perfect gas relation:

$$p_k = \rho_k R_k T_k \quad \text{for } k = A, R, P \quad (5)$$

while for DP gases, equation (2) is used. For computational cells containing a mixture of components, the perfect gas mixing relations are used. Thus the mixture temperature is calculated from:

$$T_m = [-b_m + \sqrt{b_m^2 - 4a_m(c_m - u_m)}]/2a_m \quad (6)$$

where the mixture properties are determined from:

$$a_m = \sum_k Y_k a_k, \quad b_m = \sum_k Y_k b_k, \quad c_m = \sum_k Y_k c_k, \quad R_m = \sum_k Y_k R_k \quad (7)$$

Then the mixture pressure is computed from the perfect gas relation for the mixture:

$$p_m = \rho_m R_m T_m \quad (8)$$

#### 5. TNT Combustion Revisio

We consider the combustion of TNT in an explosion of a shock-dispersed-fuel (SDF) charge consisting of a 0.5-g PETN booster surrounded by a 1.0-g TNT shell, corresponding to the experiments of Neuwald [1]. This is similar to the Aluminum combustion case considered above, with the fuel being changed from Al to TNT. In previous work [5], we considered the explosive as a pre-mixed composite charge of 33% PETN and 67% TNT, with composite EOS properties. We have detected that this led to inaccuracies (e.g., in the sound speed of the products), hence we have revised the model. We now envision a sequential detonation process: the PETN detonates; it expands and pushes on the TNT, creating a

detonation wave in the TNT; the TNT then expands and drives a blast wave into the surrounding air. The JWL constants for both explosives are listed in Table 2. In this formulation, the PETN and TNT products gases have their own (separate) EOS properties. Again we consider the PETN detonation products to be inert (i.e., non-reactive with either TNT or air), while the TNT products are assumed to be reactive, and undergo combustion when mixed with air.

Figure 5 presents the Le Chatelier diagram for detonation of TNT and PETN charges with initial density of  $\rho_0 = 1 \text{ g/cc}$ . The locus of detonation products states lie on the appropriate expansion isentrope, starting at the CJ point and expanding to 1 bar. The heats of detonation ( $-818 \text{ cal/g}$  for TNT and  $-1,423 \text{ cal/g}$  for PETN) are indicated on Fig. 5. The CJ detonation temperatures are 3,186 K and 4,600 K for TNT and PETN, respectively. Also shown are the UV points corresponding to adiabatic constant volume detonations (producing temperatures of 2,700 K and 4,223 K for TNT and PETN, respectively), and the freeze-out points (F) where the products composition becomes fixed (1,800 K). The loci are fit with quadratic functions, whose parameters are listed in Table 3.

The thermodynamic states encountered during the combustion of the TNT products with air are depicted in the Le Chatelier diagram of Fig. 6. The Reactants-R are defined as a stoichometric mixture of air and TNT *frozen* composition (air/fuel ratio:  $\sigma_s = 3.35$ ). The Products-P were assumed to be in *thermodynamic equilibrium*. These states were calculated with the Cheetah code, assuming  $p = 1 \text{ atm}$  (which we have found to adequate for perfect gases below 3,500 K). Adiabatic combustion corresponds to a material transform from Reactants to Products at constant energy. For Reactants starting at 300 K, 1,000 K and 2,000 K this gives adiabatic combustion temperatures of 2,500 K, 2,700 K and 2,900 K, respectively. The Reactants and Products loci were fit with quadratic functions, whose parameters are listed in Table 3. Heats of detonation and combustion are compared in Table 4; they are in good agreement with the calorimeter data of Ornellas [9].

The pressure-specific volume relation for TNT and PETN are compared in Fig. 7. One can see that points on the isentrope are well fit by the JWL functions shown there. Figure 8 compares  $pv/RT$  as a function of specific volume along the CJ isentrope, for PETN and TNT. One can see that for  $v > 28 \text{ cc/g}$  both products gases lie on the perfect gas relation  $pv/RT = 1$ .

## 6. Conclusions

The loci of thermodynamic states for combustion of Aluminum with air and TNT with air have been established by Cheetah code calculations. Results have been portrayed in Le Chatelier state diagram of internal energy and temperature. Results have been fit with quadratic functions  $u_k(T) = a_k T^2 + b_k T + c_k$  that accurately specify combustion states at low pressures ( $1 < p(\text{bar}) < 10$ ) and temperatures ( $T < 3,800\text{K}$ ). At small specific volumes, the JWL equation is used to calculate pressure of the detonation products, while for large specific volumes ( $v > 28\text{cc/g}$ ) the products obey the perfect gas relation. Thus, except for the very early phase of the explosion, the components behave as perfect gases. During this early phase, less than 1 percent of the fuel is consumed, so for virtually the entire combustion process, the components may be modeled as perfect gases.

## 7. References

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## ACKNOWLEDGEMENTS

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**Table 1. Thermodynamic Properties of the Component Fluids:**  $u_k(T) = a_k T^2 + b_k T + c_k$

Component $k$	$a_k$	$b_k$	$c_k$
<b>Air</b> ( $200 < T(K) < 1,000$ ) ( $1,000 < T(K) < 3,500$ )	$1.8611 \times 10^{-5}$ $6.983 \times 10^{-5}$	0.16741 0.042094	-72.198 -24.757
<b>PETN Detonation Products</b> ( $300 < T(K) < 4,600$ )	$4.0757 \times 10^{-5}$	0.17796	$-1887.3 \pm 17$
<b>Fuel: Al</b>	$\sim 0$	$\sim 0$	$\sim 0$
<b>Reactants: Al-air</b> ( $\sigma_s = 4.03$ ) ( $300 < T(K) < 4,000$ )	$8.153 \times 10^{-5}$	0.0043727	29.17
<b>Combustion Products: Al-air</b> ( $\sigma_s = 4.03$ ) ( $3,400 < T(K) < 4,000$ )	$630.85 \times 10^{-5}$	-42.63	$7.1487 \times 10^4$

**Table 2: JWL Constants for**  $p_{JWL}(v, S_{CJ}) = A \exp(-R_1 v) + B \exp(-R_2 v) + C/v^{1+\omega}$

Explosive	A (M-bar)	B (M-bar)	C (M-bar)	$R_1$ (—)	$R_2$ (—)	$\omega$ (—)	$S_{CJ}$ (cal/g - K)
<b>PETN</b> ( $\rho_0 = 1 \text{ g/cc}$ )	5.80227	0.09301	0.01223	7.00	1.695	0.246	1.96
<b>TNT</b> ( $\rho_0 = 1 \text{ g/cc}$ )	1.05515	0.01841	0.00784	4.214	1.040	0.327	1.781

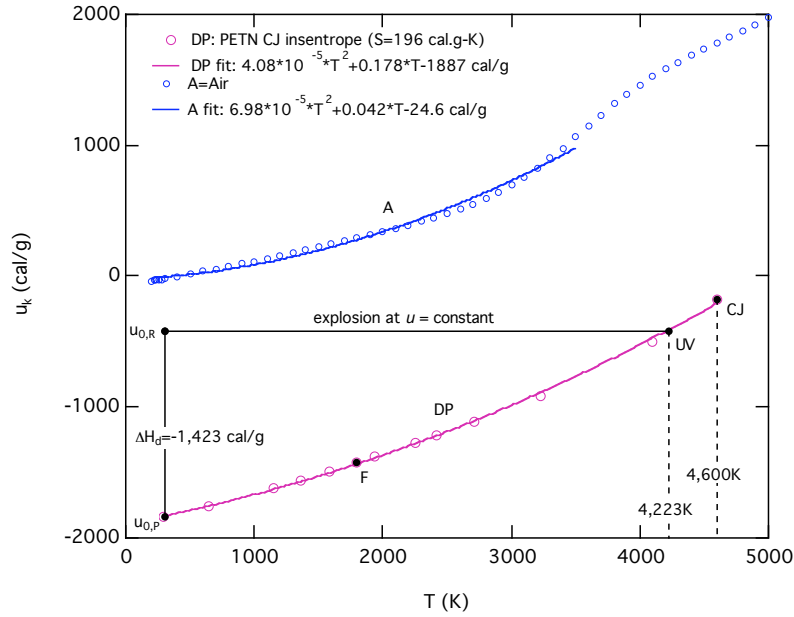
**Table 3. Thermodynamic Properties of the Component Fluids:**  $u_k(T) = a_k T^2 + b_k T + c_k$

Component $k$	$a_k$	$b_k$	$c_k$
<b>Air</b> ( $300 < T(K) < 3,500$ )	$6.983 \times 10^{-5}$	0.042094	-24.757
<b>PETN Detonation Products</b> ( $300 < T(K) < 4,600$ )	$4.0757 \times 10^{-5}$	0.17796	$-1887.3 \pm 17$
<b>TNT Detonation Products</b> ( $300 < T(K) < 3,200$ )	$5.6681 \times 10^{-5}$	0.16377	-934
<b>Reactants: TNT-air</b> ( $\sigma_s = 3.35$ ) ( $300 < T(K) < 3,200$ )	$5.627 \times 10^{-5}$	0.0921	-234
<b>Combustion Products: TNT-air</b> ( $\sigma_s = 3.35$ ) ( $1,500 < T(K) < 4,000$ )	$28.57 \times 10^{-5}$	-0.7441	-91.0

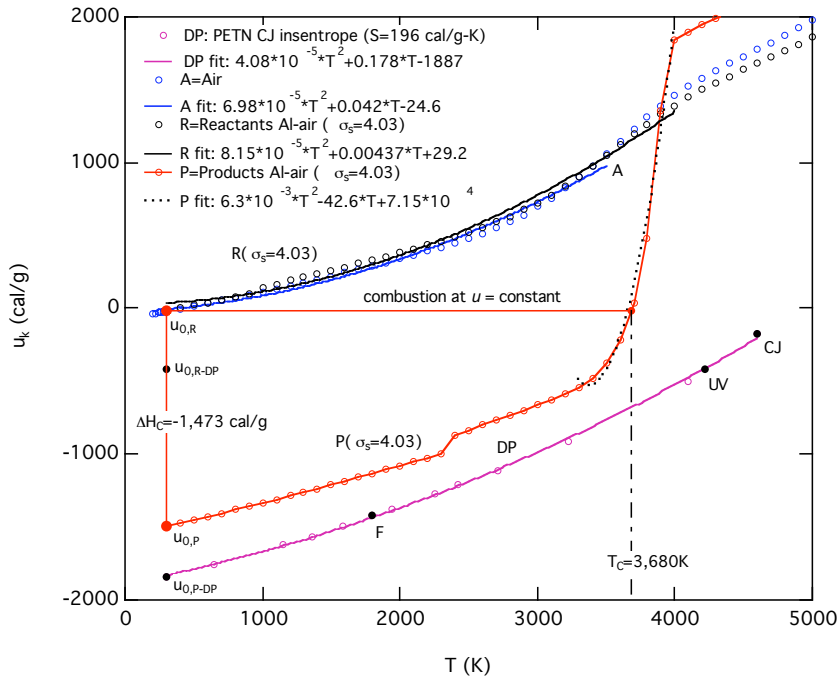
**Table 4. Heats of Detonation and Combustion for PETN, TNT and Al-air**

Fuel	$u_{0,k}$ (cal/g <sub>R</sub> )	$u_{0,DP}$ (cal/g <sub>P</sub> )	$\Delta H_d$ (cal/g <sub>R</sub> )	$u_{0,R}$ (cal/g <sub>R</sub> )	$u_{0,CP}$ (cal/g <sub>P</sub> )	$\Delta H_c$ (cal/g <sub>R</sub> )	M mol/g
<b>PETN detonation</b> ( $\rho_0 = 1 \text{ g/cc}$ )	-420.2	-1842.76	-1422.56	(—)	(—)	(—)	28.8
<b>PETN-air comb.</b> ( $\sigma_s = 0.482$ )	(—)	(—)	(—)	-278	-1649	-1371	31.62
<b>TNT detonation</b> ( $\rho_0 = 1 \text{ g/cc}$ )	-66.3	-883.79	-817.47	(—)	(—)	(—)	26.93
<b>TNT-air comb.</b> ( $\sigma_s = 3.35$ )	(—)	(—)	(—)	-31.04	-879.52	-839.48	30.05
<b>Al-air comb.</b> ( $\sigma_s = 4.03$ )	(—)	(—)	(—)	-16.143	-1489.12	-1472.98	39.15

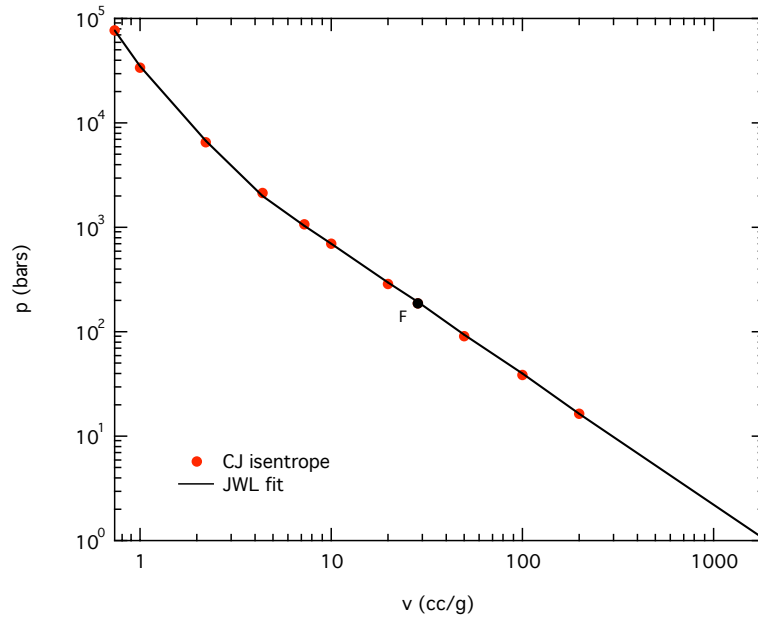




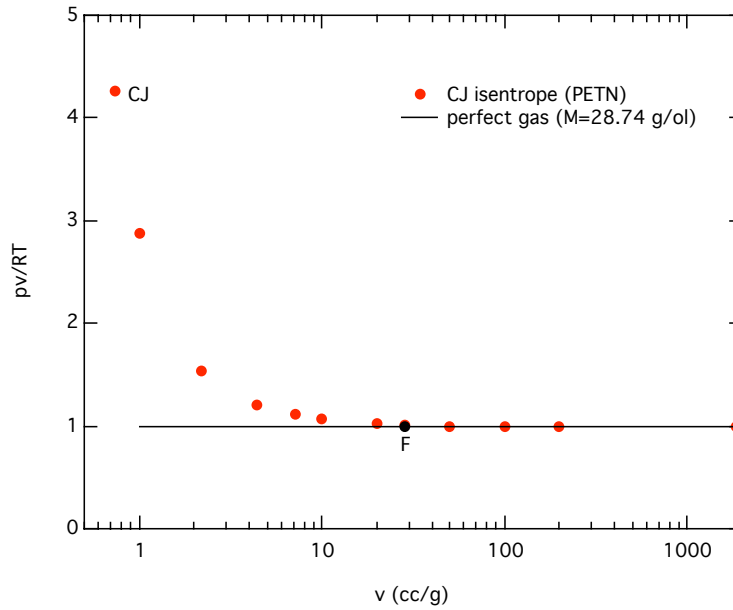
**Figure 1.** Le Chatelier diagram for detonation of a PETN charge ( $\rho_0 = 1 \text{ g/cc}$ ). Curve DP represents the locus of Detonation Products states along the expansion isentrope, starting at the CJ point, and expanding to 1 bar. Products composition becomes frozen (point F) for  $T < 1,800 \text{ K}$ . The horizontal line represents the detonation process as the transformation from Reactants-R to Detonation Products-DP at constant energy, terminating at point UV. The points are calculated with the Cheetah code, and fit with the quadratic EOS functions:  $u_k(T) = a_k T^2 + b_k T + c_k$  (see Table 1).



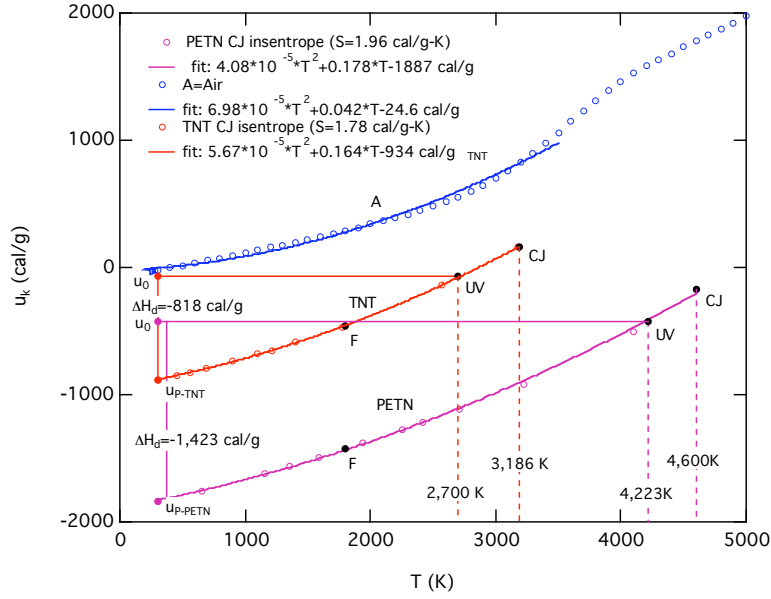
**Figure 2.** Le Chatelier diagram for stoichiometric combustion of aluminum in air ( $\sigma_{s2} = 4.03$ ). Adiabatic combustion corresponds to a material transformation from the Reactants-R to the Products-P at constant energy, represented as a horizontal line shown for reactants at 300K. The points are calculated with the Cheetah code, and fit with the quadratic EOS functions:  $u_k(T) = a_k T^2 + b_k T + c_k$  (see Table 1).



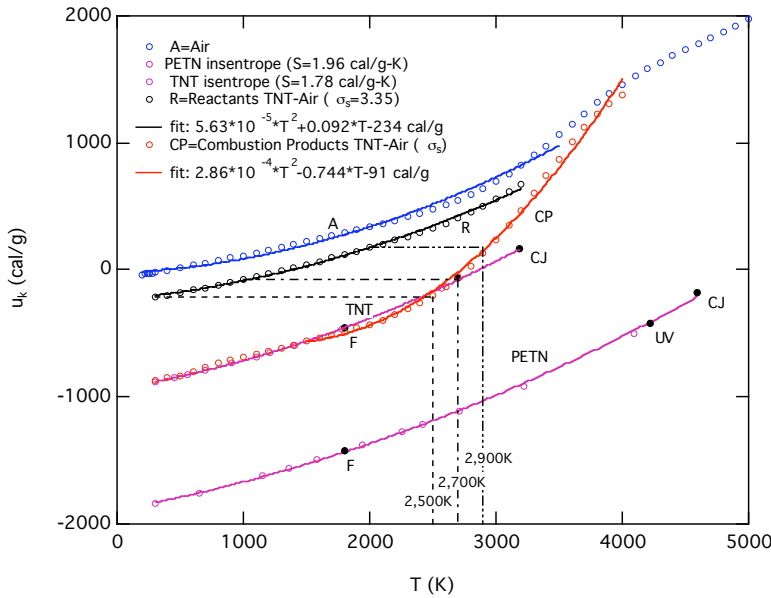
**Figure 3.** Pressure-specific volume relation (red dots) along the CJ isentrope for PETN ( $\rho_0 = 1 \text{ g/cc}$ ). The JWL function is  $p_{JWL}(v, S_{CJ}) = A \exp(-R_1 v) + B \exp(-R_2 v) + C/v^{\omega+1}$  where  $v$  represents the specific volume ratio:  $v = v/v_0$ . The JWL constants are  $A=5.80227 \text{ M-bar}$ ;  $B=0.09301 \text{ M-bars}$ ;  $C=0.01223 \text{ M-bars}$ ;  $R_1 = 7.000$ ;  $R_2 = 1.695$  and  $\omega = \gamma - 1 = 0.246$ ; they result in the fit (solid curve) shown in this figure ( $S_{CJ} = 1.96 \text{ cal/g-K}$ ).



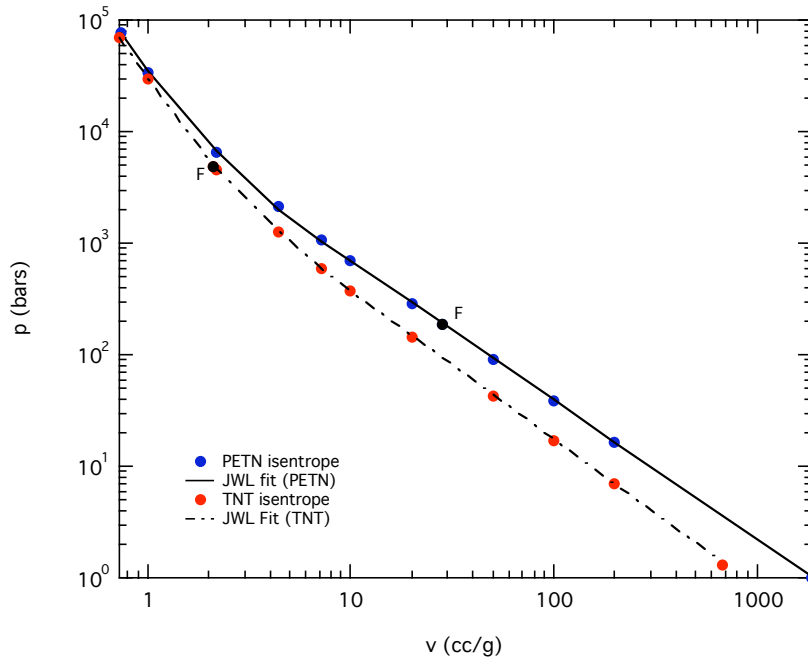
**Figure 4.** Display of  $pv/RT$  versus specific volume for detonation products gases from a PETN charge with  $v_0 = 1 \text{ cc/g}$ . The red dots are values calculated by Cheetah for the CJ isentrope. Point F denotes the volume ( $v_F = 28.3$ ) where the composition of the products becomes frozen. The solid curve represents the perfect gas relation  $pv/RT=1$ . For  $v > 28.3 \text{ cc/g}$  (or  $\rho < 35.3 \text{ g/cc}$ ), the computed points lie on that line, indicating that the detonation products behave as a perfect gas with  $R_{PETN} = R_u/M_{PETN}$  &  $M_{PETN} = 28.8 \text{ g/mol}$ .



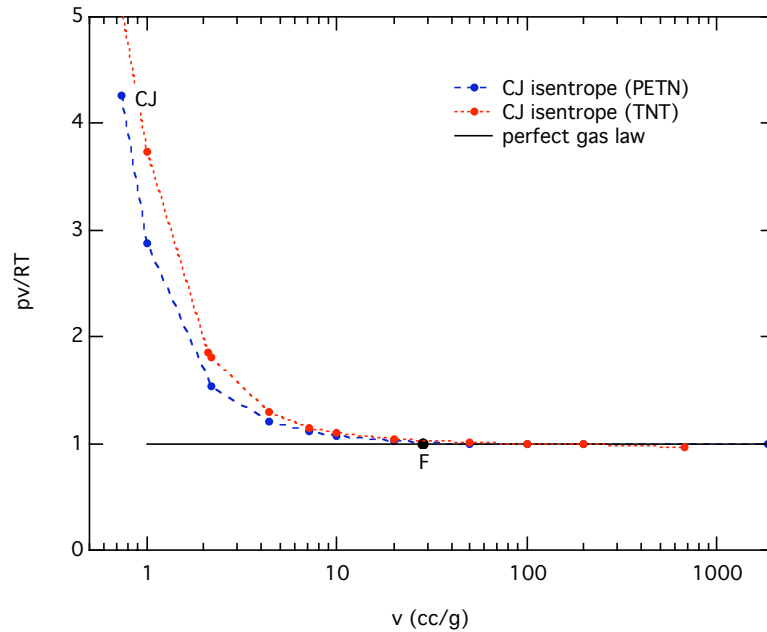
**Figure 5.** Le Chatelier diagram for detonation of TNT and PETN charges ( $\rho_0 = 1 \text{ g/cc}$ ). Curves TNT and PETN represent the locus of Detonation Products states along the expansion isentrope, starting at the CJ point, and expanding to 1 bar. Products composition becomes frozen for  $T < 1,800 \text{ K}$  (point F). The horizontal line represents the detonation process as the transformation from Reactants-R to Detonation Products-DP at constant energy, terminating at point UV. The points are calculated with the Cheetah code, and fit with the quadratic EOS functions:  $u_k(T) = a_k T^2 + b_k T + c_k$  (see Table 3).



**Figure 6.** Le Chatelier diagram for combustion of TNT detonation products gases in air (stoichiometric composition:  $\sigma_s = 3.35$ ). Adiabatic combustion corresponds to a material transformation from the Reactants-R to the Combustion Products-CP at constant energy, represented as horizontal lines shown for reactants at 300K, 1000K and 2000K. The points are calculated with the Cheetah code, and fit with the quadratic EOS functions:  $u_k(T) = a_k T^2 + b_k T + c_k$  (see Table 3).



**Figure 7.** Pressure-specific volume relation along the CJ isentrope from Cheetah (PETN & TNT at  $\rho_0 = 1 \text{ g/cc}$ ). The JWL function is  $p_{JWL}(v, S_{CJ}) = A \exp(-R_1 v) + B \exp(-R_2 v) + C/v^{\omega+1}$  where  $v$  represents the specific volume ratio:  $v = v/v_0$ . The JWL constants are listed in Table 2; they result in the fit curves shown in the figure.



**Figure 8.** Display of  $pv/RT$  versus specific volume for detonation products gases from TNT and PETN charges ( $v_0 = 1 \text{ cc/g}$ ). The dots are values calculated by Cheetah for the CJ isentrope. Point F denotes the volume where the composition of the products becomes frozen. The solid curve represents the perfect gas relation  $pv/RT = 1$ . For  $v > 28.3 \text{ cc/g}$  (or  $\rho < 35.3 \text{ g/cc}$ ), the computed points line on that line, indicating that the detonation products behave as a perfect gas. (Note that the individual gas constant  $R_k = R_u/M_k$  was used here, with  $M_{PETN} = 28.8 \text{ g/mol}$  and  $M_{TNT} = 26.925 \text{ g/mol}$ ).